MANAV RACHNA INTERNATIONAL UNIVERSITY

TITLE:SYNTHESIS AND CHARACTERIZATION OF COMPOSITE POLYMER ELECTROLYTES FILMS FOR ELECTROCHEMICAL DEVICES

Short Synopsis

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ABSTRACT

In recent years there is a huge demand of compact, lightweight, affordable, and of high capacity electronic devices. Such devices can be made by using polymer based electrolytes, which convert the chemical energy into electrical energy and have the potential to reduce energy use and dependence on fossil fuels.These polymer electrolytes show high ionic conductivity, strong solvating ability with alkali and alkaline salts and improved thermal, mechanical and electrochemical properties. The films of composite polymer electrolyte can be prepared by mixing alkali or alkaline salt with polymer and plasticizer in a fixed ratio using photo-polymerization, thermal polymerization and by sol-gel technique. The main objective of the proposed work is to prepare a new composite polymer electrolyte in film form using sol-gel technique. After synthesis and optimization of parameters, these polymer electrolyte films will be characterized by using X- Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Spectroscopy (FTIR), Impedance Analysis, Differential Scanning Calorimeter (DSC) and Cyclic Voltametery (CV).

Keywords: - Polymer Electrolytes, Composite Polymer Electrolytes, Ionic Conductivity, Electrochemical devices, Photo-polymerization, Sol-gel

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Introduction

The production, storage and distribution of energy are imperious necessities to the industry and modern society in general. Moreover, fields as aerospace, electronic circuitry or the need for new architectures for computer requires more and more devices as solid-state batteries, sensors and portable electrochemical devices. In such a context the development of solid-state electrolytes are a central challenge to be faced by scientific research by utilizing ionic salts, plasticizers, polymers, ceramics both in composite as well as in hybrid form [1-3].

In recent years, surveys have emphasized the development of solid polymer electrolytes (SPEs) as they offer some advantages under liquid electrolytes, such as higher temperatures of operation, no flowing and corrosion after damage, ease of application to electrochemical devices. As already described in many papers and books, the SPEs are solid or gel ion conducting membranes consisting of a salt dispersed in a polymer matrix forming the ionically conducting solid solution. During last two decades different systems have been extensively studied, and the most commonly studied polymer electrolytes are the complexes of Li salts with high molecular weight polyethylene oxide (PEO) [3]. PEO qualifies as a host polymer for electrolytes because of its high solvating power for lithium salts and compatibility with lithium electrode [4]. However, one of the major drawbacks of PEO based solid polymer electrolyte is their low ionic conductivity (10^{-7}-10^{-8}S/cm) at ambient temperature, which limits their practical applications [5-7]. The commonly used amorphous polymers include Poly Acrylonitrile (PAN) and Poly Methyl Methacrylate (PMMA) and the high conductivity exhibited by them is due to "gel formation", the polymer network encaging the liquid electrolyte. PMMA gel electrolytes exhibit high conductivity and good electrochemical stability; where their electrochemical stability window is reported upto 4.5V (vs Li/Li^+). PAN is reported to interact more with the liquid electrolyte taking active part in the conduction mechanism, while PMMA is regarded as more passive in nature [8, 9]. However, such plasticized film shows reasonable good conductivity but its mechanical properties decrease with increase in plasticizer content. Solid polymer electrolytes in gel form also have the problem of

leakage of plasticizer which damage the electrode as well as other components of the cell and affects the conductivity of the cell [5]. To overcome these problems, nano or submicron-sized inorganic fillers have been impregnated with polymer matrix which greatly influence the properties of polymer electrolytes [10]

Researchers have attempted many approaches for the fabrication of devices using different polymer electrolytes. In this context several attempts have been made to develop composite polymer electrolyte in film form for the ease of fabrication of device which eliminated the problems related to gel polymer electrolyte and solid polymer electrolytes [11].

Literature Review

1.Historical Survey

Electrochemistry was evolved in the 18^{th} century with the invention of 'current flow" by Luigi Galvani and "electric pile" by Alessandro Volta. Further, this electric pile or device was named as Galvanic cell and Volta was considered as "Father of Electrochemistry."

After the invention of Volta, researchers constructed these electrochemical cells in different combinations by using different electrode materials, different membranes swollen with different aqueous salt solutions. When researchers used polymer as a membrane in electrochemical cell, it shows good properties in terms of stability, durability, conductivity and better shelf life [12].

Nowadays, electrochemical cells are widely used in various electrochemical applications like in semiconductors, capacitors, electro/optical devices. Polymer based electrochemical cell have shown high performance, good ionic conduction, optically transparent and it opens the opportunities for the researchers to construct these polymer cells with different combinations for commercial purposes.

2. Electrolytes

Ionic conductivity is described as the charge movement due to the ion motion, and the phenomenon related to the electrons-holes movement into solid conductors is known as electronic conductivity. Initially ionic conduction in polymers was observed as an undesired property, but in the 1970s, this point of view was changed by Wright and co-workers when they first reported the ionic conduction in poly-ethylene oxide and alkali metal salt, [13]. Later Armand and co-workers explored the application of these materials for device application [6]. Since that time, a lot of research activities on the solid state ionic conductors have been carried out around the world to find suitable polymer electrolytes as a substitute of liquid electrolytes for the electrochemical device applications. The major problem of using polymeric electrolytes in replace of liquid or gel electrolyte is their poor conductivity as compared to liquid electrolytes. Besides improving the stability of the active interface, and also allowing a long-term durability. [14].

The use of polymer in an electrolyte can be divided into three categories, as follow: (a) a polymer containing cations or anions attached to the chain, which produces low conductivity values because of the low mobility of charge carriers (b) a polymer based electrolyte provides high values of conductivity because it is swollen with a liquid electrolyte, but does not eliminate the problems related to the liquid electrolytes; (c) a solid polymer electrolyte (when a salt is mixed with polymer) shows good ionic conductivity and better properties as compared to liquid and gel electrolytes for using them in electrochemical devices for commercial purposes. [15]

The thermodynamics of a salt dissolution are same into a polymer matrix as well as in liquid solvents. In an analysis, it is shown that the entropy of the system increases when the dissociation of salt provides the large number of particles in the system. Some differences are observed by dissolving different alkali salts in the same polymer matrix are related to the solvation energy, cohesive enthalpy of the solvent and lattice enthalpy of the salt. If the salt has high solvation energy, low cohesive enthalpy of the solvent and low lattice energy, then the dissolution and dissociation of a salt into a polymer matrix

will be more effective [15,16]. Considering these statements, the ideal candidates for dissolving a salt are the polar solvents. In the polymer chain, the salts dissociates into Lewis acids acts as cations and interact with electron donors sites and Lewis base acts as anions and interact with electron acceptor sites in the polymer chain [15].

PEO is the best reference polymer matrix for alkali salts for ionic conduction because of the oxygen atoms which has high Lewis base character. Because of this reason, great efforts have been devoted to make several alkali salts based polymer (PEO) electrolytes membrane, [17-19].

Several hypotheses have been proposed to explain the ionic motion in polymer chain. The first solid electrolyte system was based on crystalline non-processable materials, such as Li_3N, AgI and b-alumina. [20]. In PEO based system the crystalline phase is associated to its ionic conductivity. At high temperature PEO- salt based polymer electrolytes shows good conductivity [4] but below the glass transition temperature of PEO, ionic conductivity is not significant. The ionic conductivity in semi-crystalline polymer-salt complexes was assigned to the segmental motion of the amorphous phase of the polymer chains.

3. Types of polymer electrolytes

The development of polymer electrolytes are as follows: - (1) Dry Solid Polymer electrolytes, (2) gel electrolytes and (3) composite/nanocomposite polymer electrolytes. Dry solid polymer electrolytes do not contain any organic liquids and the polymer itself acts as a solid solvent along with alkali salt. The most commonly studied solid polymer electrolyte membranes are of poly ethylene oxide (PEO) with Li salts. PEO acts as a good polymer host because it has high solvating power and its good compatibility with the electrode [21]. However, it is also noticed that most PEO-Li based polymer electrolytes system shows high conductivity in the range of 10^{-3} to 10^{-4} S/cm at the temperature range of 80-100 °C but below this temperature range the electrolytes shows low conductivity values which is in the range of 10^{-7} to 10^{-8} S/cm this is because of the high crystallinity of PEO [22].

Gel electrolytes are formed by incorporating an electrolyte solution into polymer matrix. In these electrolytes the host polymer mostly provides the structural support and the liquid electrolytes produce the ion conduction. However, they show reasonable conductivity which is achieved by the use of the plasticizer, but such plasticized films shows poor mechanical properties at high plasticizer content [23]. The gel polymer electrolyte systems based on Poly (methyl methacrylate) (PMMA) because of their beneficial effects on stabilization of the lithium–electrolyte interface have been proposed for lithium battery application particularly [24]. Due to higher viscosity and lower dissociability of lithium, a decrease of ionic conductivity was observed Recently poly(vinylidenefluoride) (PVdF) as a host polymer due to its high anodic stability and high dielectric constant ($\varepsilon = 8.4$) has drawn the attention of many researchers which helps in greater ionization of lithium salts [25]. Unfortunately PVdF-based polymer electrolytes suffers leakage problem wherein the liquid component separates out from the host matrix leading to battery leak and related safety problems. Recently, poly (vinylidenefluoride-co-hexafluoropropylene) {P(VdF-HFP)} have also drawn the attention of many researchers due to their low crystallinity, glass transition temperature and high dielectric constant. P(VdF-HFP) has excellent chemical stability due to VdF unit and plasticity due to HFP unit [26]. However, plasticized P(VdF-HFP) based electrolytes exhibit drawbacks, such as increased reactivity with lithium metal electrode, solvent volatility and poor mechanical properties at high degree of plasticization [27].

In order to increase the mechanical properties of the gel polymer electrolytes by the addition of inert oxides has become an attractive approach. Due to the, enhanced ionic conductivity, electrode-electrolyte interface stability and improved mechanical stability this type of electrolytes are known as composite polymer electrolytes [28, 29]. Alternatively the concentration and particle size of the inert solid phases are helpful in increasing the ionic conductivity in composite polymer electrolytes. Generally, the larger the conductivity enhancement is achieved by using small sized particle of the oxides.

A working hypothesis has been suggested to explain the mechanism of ion transport in nano composite polymer electrolyte systems. According to this theory, the nano-fillers decrease the crystallinity of the polymer matrix as they have large surface area and it may be also due to the interaction of Lewis acid base groups of ceramics and polymer matrix. These ceramics because of the charge effects increases the amorphocity of the polymer which increases the mobility of ions and affects the conductivity of the polymer based systems. After this theory, researchers used nano-sized fillers in their research and got good results in respect of mechanical strength and conductivity. These nano fillers are divided into two classes (1) Active Ceramic fillers and (2) Passive ceramic fillers. The active material helps in the transportation of Li ions in the polymer matrix and passive materials do not involve in transport process. It has been also reported that addition of TiO2, SiO2, Al2O3, ZnS, etc. to the polymer electrolytes results in the improvements of electrochemical as well as mechanical properties [30-32]. But still the selection of fillers between active and passive components is quite arbitrary.

Now in recent years, the researchers have focused on the development of light and safe devices whose production, storage, and distribution of energy is preferentially at low cost. Therefore, the developments of new electrolytes to replace the existing traditional polymer electrolyte are obtained from finite sources. One of the possibilities is to invent new electrolytes from renewable sources and in this context, natural polymers like hydroxyl ethyl cellulose [33], starch [34] chitosan [35], agar-agar [36] pectin [37] and gelatin [38] were reported. The ionic conductivity in these system has been found in the order of 10^{-4} S/cm at room temperature. The electrochromic devices (ECDs) with good electrochromic properties have already been realized with such SPEs and they can be used in different electrochemical devices like smart windows electronic and optical devices, capacitors etc.

Description of broad area

During the last two decades, efforts are being made to produce composite polymer electrolyte by various methods like evaporation, thermal treatment and by treating with UV radiations.

Current electrolytes are still expensive and do not provide more significant energy levels. They have some drawbacks like leakage problem, they have short life, they are non-biodegradable and the main problem occurs during the filling of electrolyte in electrochemical device. To overcome from these problems we will use economical composite polymer electrolytes.

Composite Polymer electrolytes are very progressive materials. They can be prepared in semisolid or solid form, which is a cheap and reliable process when they are manufactured. Between requests for wide-usability of these electrolytes is high conductancy. Polymer electrolytes and in recent days especially composite polymer electrolytes can be used in several different cases. In accumulators and supercapacitors they can replace liquid electrolytes, as they are more stable in the meaning of chemical and electric stability and also in electrochromic displays and devices as it is very handful to prevent devices from drying out or leaking electrolyte.

Objective of the study

1. To synthesize new composite polymer electrolytes for electrochemical devices using polymers, plasticizers and ionic salts.
2. To study the electrical properties of the film by Impedance spectroscopy.
3. To study the redox behavior, working potential range of the electrolyte and the shelf life of the electrolytic film by Cyclic Voltammetry (CV).
4. To determine the amorphous or crystalline nature of polymer film by using X-Ray Diffraction (XRD).
5. To study the surface morphology by using Scanning Electron Microscopy (SEM).
6. To identify the chemical composition, chain structure and physical properties of the composite polymer film by Fourier Transform Infrared Spectroscopy (FTIR).
7. To study the heat change within the sample at varying temperature by Differential Scanning Calorimetery (DSC).

Research Methodology

1. Literature survey on the Composite Polymer Electrolytes (CPEs) for electrochemical devices.
2. Selection of polymer and salt on the basis of literature survey.
3. Synthesis of new composite polymer electrolyte by sol-gel technique with varying concentration of plasticizers, ionic salts or acids, monomer and copolymer.
4. After synthesis these films will be characterized to know the suitability of these films for electrochemical devices by using XRD, SEM, FTIR, Impedance, DSC and CV.

Expected outcomes of the research

These days, polymer gel electrolytes are being used in electrochemical devices as the third component of the devices, which also act as a separator. But these electrolytes are facing some problems of leakage from devices and even leakage of plasticizers from electrolyte's matrix with due course of time. Such problems can be minimized or overcome by the use of CPE films into electrochemical devices. These films will definitely favor ease of lamination and hermetic sealing of electrochemical devices.

Internationally, many reports are available on Solid polymer electrolytes (SPEs), few on CPEs but very few ones on Nano-CPEs films. Initial attempts have been made to synthesize films of HEMA based CPE using photo- polymerization technique. These films have shown remarkable properties in comparison to existing composite polymer electrolytes.

The anticipated research outcome of the proposed research would be the availability of a scientific database containing design, characterization and fabrication of a new technique based composite polymer electrolytes and Nano-CPE films and of technical data regarding their device applications. Thus, the proposed work is aimed towards exploration of patent- able components of the research outcome at every stage of the investigation followed by dissemination of those publishable results in national and international journals in the field of Solid State Ionics. These polymerized films will definitely replace the existing solid polymer electrolytes or composite polymer electrolytes and full fill the requirements of electrochemical device industries.

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